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(54) **[Title of the Invention]** Soiling-Resistant Soft Contact Lens Material

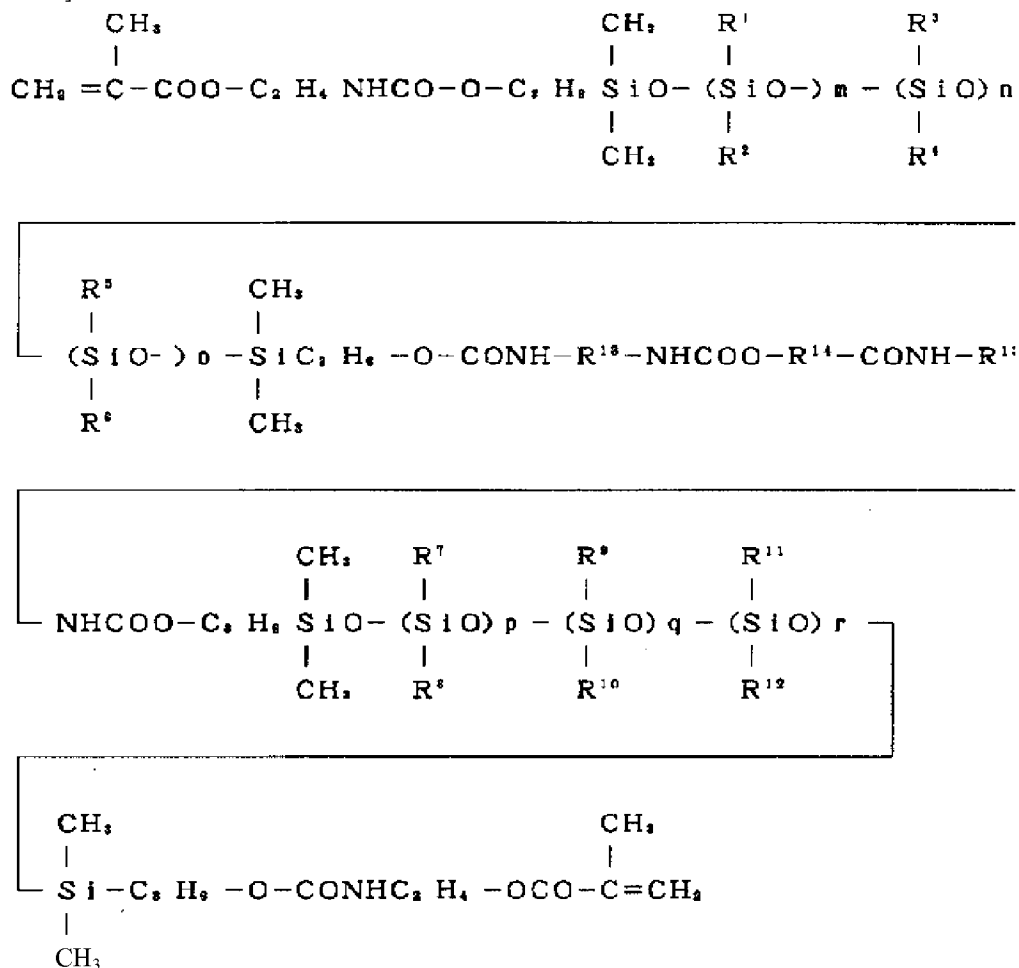
(57) **Abstract**

**[Problem]** To provide a water-containing soft contact lens material to which little there is little attachment of proteins and lipids and which has a superior oxygen permeation coefficient (DK value), optical and mechanical properties.

**[Means of Solution]** A contact lens material that is comprised of a polymer that is obtained by polymerizing one or two or more bifunctional organic siloxane macromers that are represented by a specified general formula with said bifunctional organic siloxane macromers only or together with one or two or more monomers that can be copolymerized.

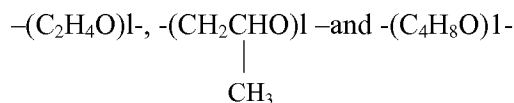


[Chemical Formula 2]



[Wherein,  $\text{R}^1, \text{R}^2, \text{R}^5, \text{R}^6, \text{R}^8, \text{R}^{11}$  and  $\text{R}^{12}$  are groups selected from  $-\text{CH}_3$  and  $-\text{CH}_2\text{CH}_2\text{CF}_3$  and may be the same or different;  $m, o, p$  and  $r$  are integers in the range of 5 to 30;  $\text{R}^3, \text{R}^4, \text{R}^9$  and  $\text{R}^{10}$  are groups selected from  $-\text{CH}_3$ ,  $-(\text{CH}_2\text{CH}_2\text{O})_s\text{CH}_2$  and may be the same or different;  $n$  and  $q$

are integers in the range of 0 to 30;  $s$  is an integer in the range of 1 to 20;  $\text{R}^{13}$  is a group selected from hexamethylene groups, tetramethylene groups, cyclohexylmethane groups, hydrogenated tolylene groups, hydrogenated xylylene groups and isophorone groups;  $\text{R}^{14}$  is a group selected from



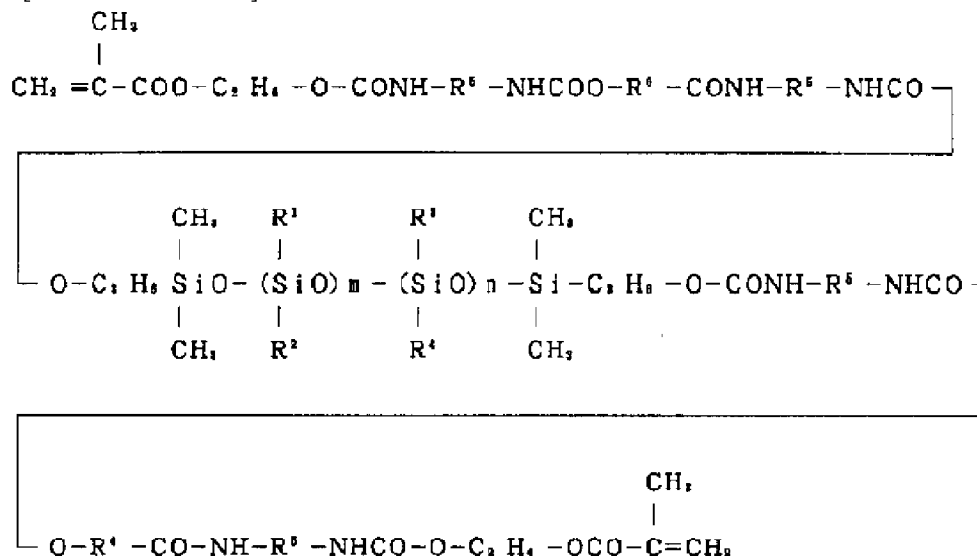
and  $l$  is an integer in the range of 1 to 20.

**[Claim 3]** A contact lens material as described in Claims 1 and 2 in which the organic siloxane macromer described in

Claim 1 is a bifunctional organic siloxane macromer as represented by Chemical Formula 3 below.

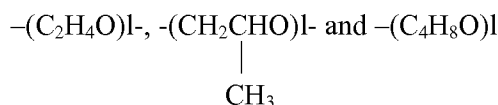
**[Chemical Formula 3]**

[Chemical Formula 3]



[Wherein,  $\text{R}^1$ , and  $\text{R}^2$  are groups selected from  $-\text{H}$ ,  $-\text{CH}_3$  and  $-\text{CH}_2\text{CH}_2\text{CF}_3$  and have at least one  $-\text{CH}_3$  group;  $m$  is an integer in the range of 5 to 50;  $\text{R}^3$  and  $\text{R}^4$  are groups selected from  $-\text{CH}_3$  and  $-\text{CH}_2\text{CH}_2\text{CF}_3$  and have at least one  $-\text{CH}_2\text{CH}_2\text{CF}_3$  group;  $n$  is an integer in the range of 0 to 50;  $\text{R}^5$

is a group selected from hexamethylene groups, tetramethylene groups, dicyclohexylmethane groups, hydrogenated tolylene groups, hydrogenated xylylene groups and isophorone groups.  $\text{R}^6$  is a group elected from



and  $\text{l}$  is an integer in the range of 1 to 20.

**[Claim 4]** A contact lens material that is comprised of copolymers that contain one or two or more substances selected from organic siloxane macromers that contain at least one of the bifunctional organic macromers represented by Chemical Formula 1, and methacrylic acid siloxanyl alkyl esters, acrylic acid fluoroalkyl esters, methacrylic acid fluoroalkyl esters, acrylic acid alkyl esters and methacrylic acid alkyl esters of alkyl groups having hydroxyl groups, N,N'-dimethyl acrylamide, N-vinyl pyrrolidone, ethylene glycol dimethacrylate and tetraethylene glycol dimethacrylate.

#### [Detailed Description of the Invention]

[0001]

**[Technological Field of the Invention]** This invention relates to a novel contact lens material. Speaking in greater detail, this invention relates to a soft contact lens material which exhibits little attachment of soiling such as the proteins and lipids in tears and which exhibits a superior balance of physical properties such as oxygen permeability.

[0002]

**[Prior Art]** Soft contact lenses can be divided into water-containing soft contact lenses and water non-containing soft contact lenses. Water-containing soft contact lenses are comprised of copolymers that are obtained by polymerizing hydrophilic monomers such as hydroxyethyl methacrylate

and N-vinyl pyrrolidone as the principal constituents. The lenses are made by the cutting or casting methods and the lenses, which have been subjected to swelling treatment with physiological saline solution have a water content ratio of approximately 40 to 70%.

**[0003]** Known non-water containing soft contact lenses include, for example, silicone rubber lenses that are obtained by a method in which a platinum catalyst is added to a mixture of polydimethylene siloxane and methyl hydrodiene polysiloxane of which both terminals of the molecular chain are blocked by vinyl dimethyl silyl groups and the mixture is heated and hardened by the molding method and flexible lenses of which the principal constituent is polyperfluoroether to the two terminals of which have been added polymerizable groups such as methacryloxy groups and which have a modulus of elasticity intermediate between those of soft contact lenses and hard contact lenses (Japanese Patent Application Early Disclosure No. Sho 54-81363 [1979] and Japanese Patent Application Early Disclosure No. Sho 58-127914 [1983]). In addition, non-water-containing soft contact lenses of excellent wearing feel can also be manufactured by cutting from a hard substrate in which (meth) acrylic acid and an acrylic acid ester have been copolymerized to make a lens, which lens is then subjected to esterification or ester interchange treatment (Japanese Patent Application Early Disclosure No. Sho 48-75047 [1973]).

[0004] Contact lens materials of high oxygen permeability of which polyfunctional polysiloxanes are the principal constituents have been disclosed in Japanese Patent Application Early Disclosure No. Sho 54-24047 [1979], Japanese Patent Application Early Disclosure No. Sho 56-51715 [1981], Japanese Patent Application Early Disclosure No. Sho 59-229524 [1984] and Japanese Patent Application Early Disclosure No. Hei 2-188717 [1990]. Water-containing soft contact lenses have the advantages that they are soft and of excellent wearing feel and that they have high oxygen permeability when they are of a high water content type. However, they are easily damaged, are of poor durability are easily contaminated by components of tears and there is the danger of growth of bacteria, for which reason they must be periodically boiled and disinfected and there are many inconveniences in handling. The following problems are seen with non-water-containing contact lenses.

[0005] First, silicone rubber contact lenses have the drawback that they adhere to the cornea because the layer that had been subjected to hydrophilic treatment, which is performed on initial development to improve the hydrophobicity of the lens surface, is peeled off and its elasticity becomes excessively great. They have not yet reached the level of widespread practical use. Although most recently there has been some improvement in the above described drawbacks as the result of advances in surface hydrophilic treatment, changes in lens design and improvements in mechanical properties, they are still not sufficiently satisfactory and have not reached the point of widespread general use.

[0006] Next, because non-water-containing lenses of which polyperfluoroether is the principal constituent are closer to the semi-hard type than soft contact lenses, a wearing feel like that of soft contact lenses is not obtained and movement

of the lens on the cornea is not satisfactory. In addition, soft contact lenses of which (meth) acrylic acid esters are the principal constituents have poor oxygen permeability and are not suited to wearing for long periods. Materials of which polyfunctional polysiloxanes are the principal constituents are materials that are close to silicone rubber lenses, not taking into consideration contamination by components of tears.

[0007]

**[Problems the Invention is Intended to Solve]** This invention has the objective of providing, on the basis of these facts, a water-containing soft contact lens with which there is little soiling attachment of proteins and lipids and that has a superior oxygen transmission coefficient (DK value) and optical and mechanical properties.

[0008]

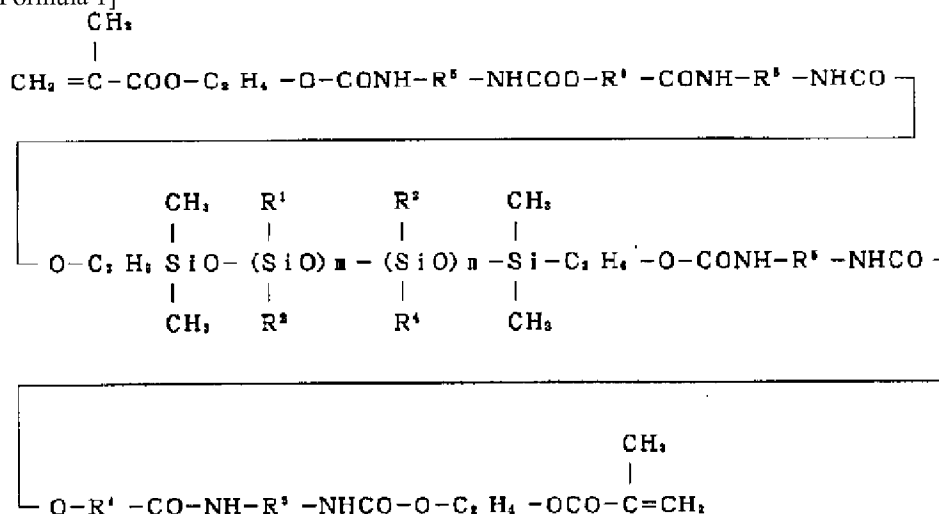
**[Means for Solving the Problems]** The inventors conducted repeated and intensive research for the purpose of developing a soft contact lens material with which the above-described problems could be solved. As the result, they discovered that this objective could be achieved by means of a material comprised of copolymers obtained by polymerizing bifunctional organic siloxane macromers having a specified structure and molecular weight as the principal constituents and perfected this invention on the basis of this finding.

1. A contact lens material that is comprised of a polymer that is obtained by polymerizing one or two or more bifunctional organic siloxane macromers that are represented by chemical formula 1 below with said bifunctional organic siloxane macromers only or together with one or two or more monomers that can be copolymerized.

[0009]

**[Chemical Formula 4]**

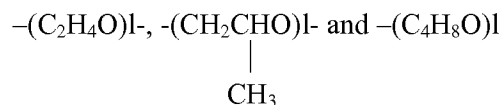
[Chemical Formula 1]



[0010]

[Wherein,  $\text{R}^1$ , and  $\text{R}^2$  are groups selected from  $-\text{H}$ ,  $-\text{CH}_3$  and  $-\text{CH}_2\text{CH}_2\text{CF}_3$  and have at least one  $-\text{CH}_3$  group;  $m$  is an integer in the range of 5 to 100;  $\text{R}^3$  and  $\text{R}^4$  are groups selected from  $-\text{CH}_3$  and  $-\text{CH}_2\text{CH}_2\text{CF}_3$  and have at least one

$\text{CH}_2\text{CH}_2\text{CF}_3$  group;  $n$  is an integer in the range of 0 to 50;  $\text{R}^5$  is a group selected from hexamethylene groups, tetramethylene groups, dicyclohexylmethane groups, hydrogenated tolylene groups, hydrogenated xylylene groups and isophorone groups.  $\text{R}^6$  is a group elected from



and  $\text{l}$  is an integer in the range of 1 to 20.

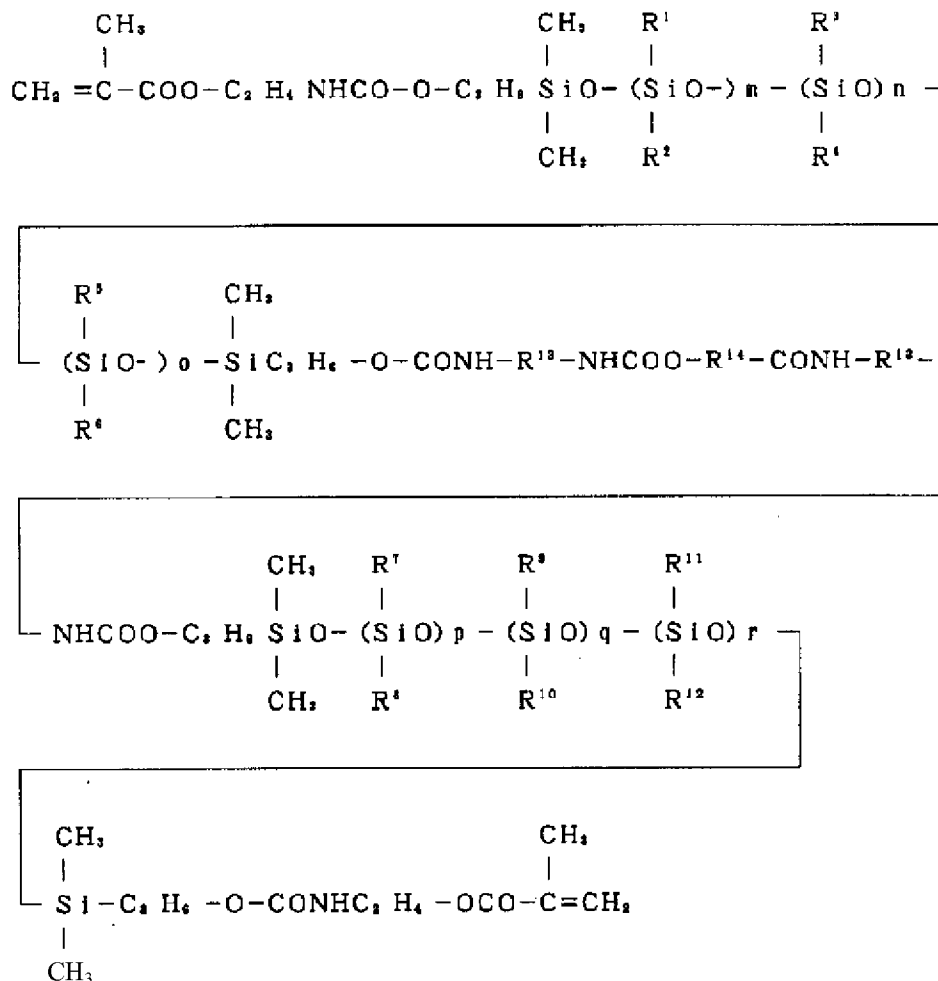
2. A contact lens material in which the bifunctional organic siloxane macromer is a polymer that is obtained by polymerizing only a bifunctional organic siloxane macromer which is a mixture of one or two or more substances represented by Chemical Formula 1 as described in 1 above

and one or two or more of the substances indicated by Chemical Formula 2 below or together with one or two or more monomers that can be copolymerized.

[0011]

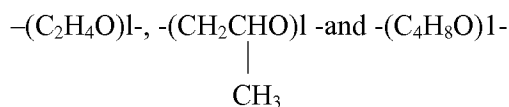
[Chemical Formula 5]

[Chemical Formula 2]



[0012] [Wherein,  $\text{R}^1, \text{R}^2, \text{R}^5, \text{R}^6, \text{R}^7, \text{R}^8, \text{R}^{11}$  and  $\text{R}^{12}$  are groups selected from  $-\text{CH}_3$  and  $-\text{CH}_2\text{CH}_2\text{CF}_3$  and may be the same or different;  $m, o, p$  and  $r$  are integers in the range of 5 to 30;  $\text{R}^3, \text{R}^4, \text{R}^9$  and  $\text{R}^{10}$  are selected from  $-\text{CH}_3, -(\text{CH}_2\text{CH}_2\text{O})_s\text{CH}_3$  and may be the same or different;  $n$  and  $q$

are integers in the range of 0 to 30;  $s$  is an integer in the range of 1 to 20;  $\text{R}^{13}$  is a group selected from hexamethylene groups, tetramethylene groups, cyclohexylmethane groups, hydrogenated tolylene groups, hydrogenated xylylene groups and isophorone groups.  $\text{R}^{14}$  is a group selected from



and  $l$  is an integer in the range of 1 to 20.]

[0013] The  $\text{R}^5$  group in Chemical Formula 1 and the  $\text{R}^5$  group in Chemical Formula 2 are residues of bifunctional isocyanates and may include, for example, residues of hexamethylene diisocyanate, tetramethylene diisocyanate, 2,4,4-trimethyl-1,6-hexamethylene diisocyanate, 2,6-diisocyanatomethyl caproate, 3-isocyanatomethyl-3,5,5-trimethyl cyclohexyl isocyanate, dicyclohexylmethane-4,4'-diisocyanate, hydrogenated xylylene diisocyanate, hydrogenated tolylene diisocyanate, and isophorone

diisocyanate, of which residues of hexamethylene diisocyanate and isophorone diisocyanate are desirable in terms of the balance of the mechanical properties of the lens. The  $\text{R}^6$  group and the  $\text{R}^{14}$  group are residues of polyoxyethylene glycols, and include, for example, residues of polyethylene glycol, polypropylene glycol and polytetraethylene glycol. Substances of a degree of polymerization in the range of 1 to 20 can be used. Of these, polyethylene glycol is preferable because of its superior

aqueous wetting properties and properties of preventing soiling attachment to the lens.

**[0014]** The bifunctional organic siloxane macromers represented by Chemical Formula 1 are obtained, for example, by reacting an excess quantity of 2-hydroxyethyl methacrylate with 1,3-bis-(hydroxypropyl) tetramethyl disiloxane and octamethethyl cyclotetrasiloxane, and, in some cases, with a diol having the polysiloxane structure obtained by ring-opening insertion reactions of 1,3,5-trifluoropropyl trimethyl cyclotrisiloxane, with a product obtained by reacting an excess quantity of a terminal modified isocyanate of polyethylene guticol obtained, for example, by reacting twice its volume of hexamethylene diisocyanate. The structures of the bifunctional organic siloxane macromers that have been obtained in this way were analyzed from their NMR (nuclear magnetic resonance spectra) and IR absorption spectra.

**[0015]** The structural ratios of the dimethyl siloxane structure and the methyl trifluoropropyl siloxane structure of the polysiloxane structure were found by determining the integration value of proton absorption relevant to the methyl groups and of proton absorption relevant to the trifluoropropyl groups that appeared on the NMR spectra and by determining the integration values of proton absorption relevant to the methylene groups contained in the same molecules. Of these bifunctional organic siloxane macromers, the macromers of diols having a polyfluorosiloxane structure obtained by ring-opening insertion reactions of 1,3-bis-(hydroxypropyl) tetramethyl disiloxane and octamethethyl cyclotetrasiloxane, in some cases, 1,3,5-trifluoropropyl trimethyl cyclotrisiloxane have superior effects in preventing soiling attachment of proteins and lipids

**[0016]** The bifunctional organic siloxane macromers represented by Chemical Formula 2 are obtained, for example, by reacting a 1,3-bis-(hydroxypropyl) tetramethyl disiloxane and octamethethyl cyclotetrasiloxane, and, in some cases, with a terminal modified isocyanate of polyethylene guticol obtained by reacting hexamethylene diisocyanate with twice its volume of diol having the polysiloxane structure obtained by ring-opening insertion reactions of, in some cases, 1,3,5-trifluoropropyl trimethyl cyclotrisiloxane, for example, twice its volume of polyethylene glycol and by further reacting 2-isocyanato ethyl methacrylate. The structures of the bifunctional organic siloxane macromers that have been obtained in this way were analyzed from their NMR (nuclear magnetic resonance spectra) and IR absorption spectra.

**[0017]** The structural ratios of the dimethyl siloxane structure and the methyl trifluoropropyl siloxane structure of the polysiloxane structure were found by determining the integration value of proton absorption relevant to the methyl groups and of proton absorption relevant to the trifluoropropyl groups that appeared on the NMR spectra and by determining the integration values of proton absorption relevant to the methylene groups contained in the same molecules. The contact lenses of this invention are comprised of cross-linked polymers obtained by

copolymerizing one or two or more of the bifunctional organic siloxane macromers represented by Chemical Formula 1 with only said bifunctional organic siloxane macromers or with one or two or more copolymerizable monomers. The type and binding number of the structural units that constitute the  $R^6$  group and the residues that constitute the  $R^5$  group in chemical formula 1 are selected depending on the target properties of the contact lens, for example, the required oxygen permeability, softness, difficulty of soiling attachment and strength.

**[0018]** We shall now explain the copolymerizable monomers. The methacrylic acid siloxanyl alkyl esters that are used as the copolymerizable monomers in this invention are the above described siloxane macromers and substances that improve the oxygen permeability of the lens and have the effects of aiding the compatibility of the monomers and macromers described below and of increasing the light ray transmission ratio of the lens. For example, one or two or more can be selected from tris(trimethylsiloxy) silyl propyl methacrylate, bis(trimethylsiloxy)methyl silyl propyl methacrylate, pentamethyl disiloxane propyl methacrylate, tris(trimethylsiloxy) silyl propyloxyethyl methacrylate, and tris(polydimethylsiloxy) silyl propyl methacrylate.

**[0019]** The acrylic acid fluoroalkyl esters and methacrylic fluoroalkyl esters that are used as the copolymerizable monomers in this invention have the properties of water repellency and oil repellency due to decrease in critical surface tension attributable to their fluorine atoms. These properties have the effect of inhibiting contamination of the surface of the contact lens by such constituents of tears as proteins and lipids. In terms of physical properties, it is further desirable that the glass transition point of the monomer constituent be below room temperature so that the softness and flexibility required of soft contact lenses when it is copolymerized will be manifested.

**[0020]** Specific examples of these acrylic acid fluoroalkyl esters and methacrylic fluoroalkyl esters can include trifluoroethyl acrylate, tetrafluoroethyl acrylate, tetrafluoropropyl acrylate, pentafluoropropyl acrylate, hexafluorobutyl acrylate, hexafluoroisopropyl acrylate, heptafluorobutyl acrylate, octafluoropentyl acrylate, nonafluoropentyl acrylate, dodecafluoropentyl acrylate, dodecafluorobutyl acrylate, dodecafluorooctyl acrylate, tridecafluoroheptyl acrylate and methacrylate corresponding to these acrylates, and, preferably, with trifluoroethyl acrylate, hexafluoroisopropyl acrylate, octafluoropentylacrylate and dodecafluorooctyl acrylate being used. One of these monomers may be used and combinations of two or more may also be used.

**[0021]** In addition, the acrylic acid alkyl ester monomers and methacrylic acid alkyl ester monomers that are used as copolymerizable monomers in this invention have the effect of improving the compatibility of the bifunctional organic siloxane macromers and the (meth) acrylic acid fluoroalkyl esters and play a role in greatly broadening the range of use. Preferably, it is desirable that they be substances that lower the glass transition point of the copolymer to room

temperature or to 0°C or lower. Thereby, they have the effect of conferring elasticity and softness on the copolymer.

**[0022]** Specific examples of these acrylic acid alkyl esters and methacrylic acid alkyl esters can include methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, tert-butyl acrylate, isobutyl acrylate, n-hexyl acrylate, n-octyl acrylate, n-heptyl acrylate, n-nonyl acrylate, n-decyl acrylate, isodecyl acrylate, n-lauryl acrylate, tridecyl acrylate, n-docecyl acrylate, cyclopentyl acrylate, cyclohexyl acrylate, n-acetyl acrylate and methacrylates corresponding to these acrylates. Preferably, n-butyl acrylate, n-octyl acrylate, n-lauryl methacrylate and n-stearyl methacrylate are used. One of these monomers may be used or two or more may be used in combination.

**[0023]** As desired, the monomers indicated below can be copolymerized for the purpose of improving mechanical properties, surface wettability and the dimensional stability of the lens. Monomers for improving mechanical properties include, for example, aromatic vinyl compounds such as styrene, tert-butyl styrene and  $\alpha$ -methyl styrene. Monomers for improving surface wettability include, for example, methacrylic acid, acrylic acid, itaconic acid, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl methacrylate, 2-hydroxypropyl acrylate, glycerol methacrylate, polyethylene glycol methacrylate, N,N'-dimethyl acrylamide, N-methyl acrylamide, dimethyl aminoethyl methacrylate, methylene bisacrylamide, diacetone acrylamide and N-vinyl pyrrolidone.

**[0024]** Monomers for improving the dimensional stability of the lens can include, for example, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, trimethylol propane trimethacrylate, pentaerythritol trimethacrylate, acryl methacrylate and acrylates corresponding to these methacrylates. One of these monomers may be used or two or more of them may be used in combination. Mixed monomers in which copolymerizable monomers are combined can be used for the purpose of improving the balance of such properties as optical properties, oxygen permeability, mechanical strength, deformation recovery capacity, soiling attachment when worn in the eyes, dimensional stability in tears and changes in them over time.

**[0025]** Examples of mixed monomers that are copolymerizable with the bifunctional organic siloxane macromers of this invention include combinations of tris (trimethylsiloxy) silyl propyl methacrylate, trifluoroethyl methacrylate, N-vinyl pyrrolidone, N,N'-dimethyl acrylamide and ethylene glycol dimethacrylate, and combinations of N-vinyl pyrrolidone, N,N'-dimethyl acrylamide and ethylene glycol dimethacrylate. The copolymers that are used as the contact lens materials of this invention can be molded into contact lenses by the cast polymerization method in which a mold is filled with the monomer mixture which is then subjected to radical polymerization by a known method, a method in which the monomer mixture is charged into a rotating hemihedral mold and is polymerized, or a method in which the copolymer is

frozen and cut at a low temperature. The copolymerization methods that can be used include a method in which a photopolymerization initiator such as benzoin, benzophenol or benzyl dimethyl ketanol is present in the monomer mixture and polymerization is effected by irradiation with ultraviolet rays or a method in which thermal polymerization is performed using azo compounds and organic compounds such as azobisisobutyronitrile, benzoyl peroxide and lauroyl peroxide.

#### **[0026]**

**[Working Examples]** Next, we shall present a more detailed explanation of this invention by means of working examples. However, this invention is not limited in any way by these examples. The various physical properties were found as follows.

#### **(1) Oxygen Permeability Coefficient**

A K-316 · IPI gas permeability determination device manufactured by the Rika Seiki Industrial Company (Ltd.) was used. A test material strip in the shape of a lens of a diameter of 13.5 mm and a thickness of 0.09 mm was used for the determination and the oxygen permeability coefficient was calculated from the slope the straight line on the chart. Determinations were performed at 35°C. The numerical value was indicated by  $\times 10^{-11}$  (ml · cm/cm<sup>2</sup> · sec · mmHg).

#### **[0027] (2) Contact Angle**

A "Contact Angle Meter Model CA-DT" manufactured by the Kyowa Surface Science Company (Ltd.) was used. The test material strips were used in the determinations after having been immersed for 24 hours in purified water before the determinations. In the determination, the test material strip was allowed to stand in purified water and air bubbles of 1.5 to 2.0 mm in diameter were brought into contact with the bottom face of the test material strip by means of a syringe. The angle of contact that the air bubbles and the test material strip formed was read and the angle of contact was found by calculation.

#### **3) Tensile Strength**

An SV-50 universal tensile compression testing machine manufactured by Shimazu Seisakujo was used. The test material strips were supplied to the determinations as samples cut to a width of 5.0 mm. The drawing speed was 10 mm/minute. Three determinations were performed for the same test material strip and tensile strength was found from the values that were obtained by the calculation method described in JIS-K-6301.

#### **[0028] 4) Soiling Attachment Capacity**

Attachment capacity of proteins

A model soiling aqueous solution having the composition described below was mixed.

NaCl	0.9 wt%
NaH <sub>2</sub> PO <sub>4</sub>	0.0184 wt%
Na <sub>2</sub> HPO <sub>4</sub>	0.076 wt%
Egg white lysozyme	0.12 wt%
Bovine serum albumin	0.388 wt%
CaCl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	0.0407 wt%



One lens was introduced into 2 ml of this solution and was soaked in it for 24 hours at a temperature of 37°C. The lens was then introduced into purified water and was shaken and washed for 30 minutes. The lens was removed and the surface water was gently wiped off. The lens was immersed in a protein analysis reagent (BCA solution) solution (1 lens/2 ml) and a reaction was carried out for 5 hours at 40°C, after which determinations were made at UV 562 nm with a spectrophotometer (Model V-550, manufactured by Nippon Bunko Co. (Ltd.)). The mass of attached protein per lens was found from a calibration curve that had been found separately.

#### [0029] Attachment Capacity of Lipids

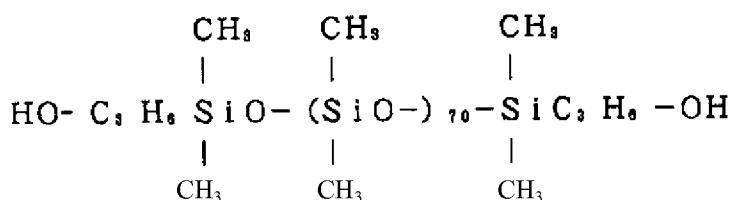
A 1% phosphate buffer solution of olive oil was stirred and mixed, the lens was introduced and was immersed in it for 23 hours in a constant temperature tank at 40°C. The lens was then introduced into a vessel into which 5 ml of purified water had been introduced and shaking and washing were carried out for 30 seconds. This washing was repeated 5 times. The lens was vacuum dried, after which extraction was performed with a mixed solvent of chloroform/methanol : 2/1, coloration was effected with triglyceride G test solution and absorbance was determined with a spectrophotometer (Model V-550, manufacture by Nippon Bunko Co. (Ltd.)). The quantity of attached lipid per lens was found from a calibration curve that has been found separately.

#### (5) Water Content Ratio

The test material was immersed for 72 hours in purified water at 37°C, the water on the surface was gently wiped off and weight was precisely measured, after which it was dried in a vacuum dryer until a constant weight was reached.

Water content ratio = (weight change/weight before drying) × 100

[Chemical Formula 4]



After cooling, the product was washed with methanol, the unreacted raw materials were extracted, the organic macromer layer was separated, activated carbon for decolorization and magnesium sulfate for dehydration were added and the mixture was allowed to stand overnight. Following that, the mixture was filtered with an 0.2 μ Teflon filter, after which the low boiling point substances were removed using an evaporator. When this was done, 71.6 g of

#### [0030]

**[Working Example 1]** 100 g (0.5 mol) of polyethylene glycol of molecular weight 200 was charged into a 500 ml brown, round-bottom flask equipped with a condenser, a thermometer and a stirrer, 201.6 g (1.2 mol) of hexamethylene diisocyanate was added, 5 drops of dibutyltin dialaurate and tetrahydrofuran were added, and, as the mixture was being stirred in a nitrogen atmosphere, a reaction was carried out for 5 hours at 70°C. During the reaction, changes in absorption were followed by means of the infrared absorption spectrum on the basis of the mixture was being stirred in a nitrogen atmosphere, a reaction was carried out for 5 hours at 70°C. During the reaction, changes in absorption were followed by means of the infrared absorption spectrum on the basis of the isocyanate groups and elimination in changes in absorption was confirmed.

**[0031]** 156.7 g (0.1 mol) of organic siloxane diol as represented by Chemical Formula 4 below and having hydroxyl groups in both terminals was charged into a 500 ml brown, round-bottom flask equipped with a condenser, a thermometer and a stirrer, 107.2 g (0.2 mol) of the above described diisocyanate compound was added, 5 drops of butyltin dilaurate and tetrahydrofuran were added, and as the mixture was being stirred in a nitrogen atmosphere, a reaction was carried out for 5 hours at 70°C. During the reaction, changes in absorption were followed by means of the infrared absorption spectrum on the basis of the isocyanate groups. In addition, 37.2 g (0.24 mol) of 2-hydroxyethyl methacrylate was added dropwise, the reaction was continued and changes in absorption were followed by means of the infrared absorption spectrum on the basis of the isocyanate groups.

#### [0032]

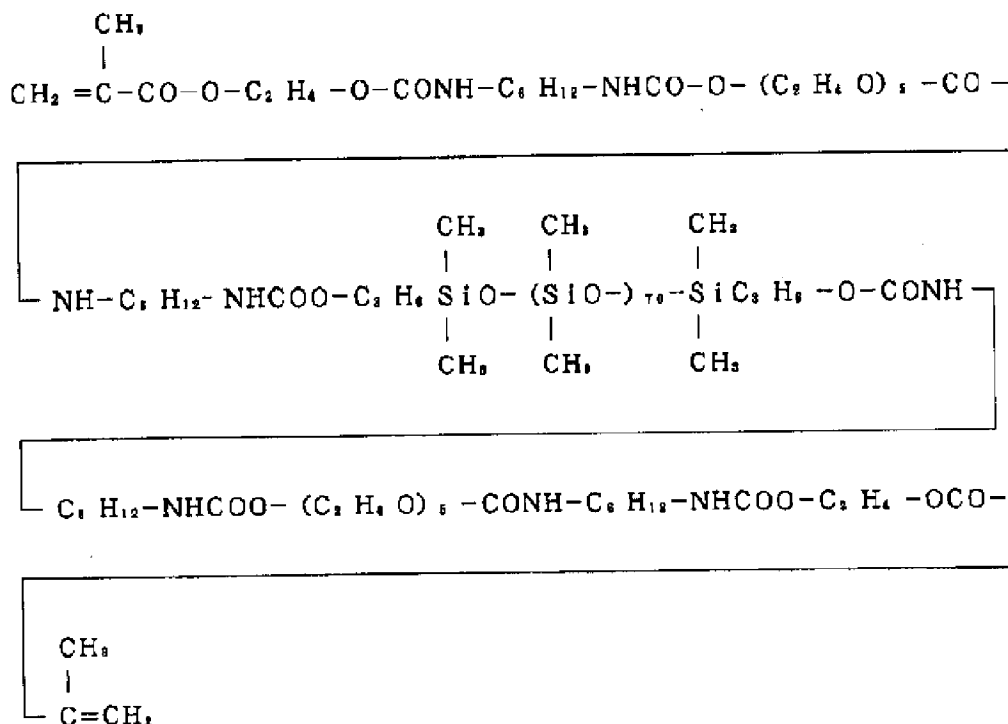
**[Chemical Formula 6]**

a transparent, slightly viscous liquid was obtained. The structure of this liquid was analyzed by NMR (proton nuclear magnetic resonance spectrum). As the result, it was confirmed that it was an organic siloxane macromer as represented by Chemical formula 5 below.

#### [0033]

**[Chemical Formula 7]**

[Chemical Formula 5]



[0034] 55 parts by weight of the organic siloxane macromer containing urethane bonds indicated by Chemical Formula 5, 15 parts by weight of tris(trimethylsiloxy) silyl propyl methacrylate, 15 parts by weight N,N-dimethyl acrylamide, 5 parts by weight of trifluoroethyl methacrylate, 1 part by weight of ethylene glycol dimethacrylate and 0.5 parts by weight of benzoyl dimethyl ketanol (brand name: I-651), manufactured by the Ciba-Geigy Company) were added, and the mixture was dissolved and mixed by stirring 1 hour in a nitrogen atmosphere with a magnetic stirrer. Following that, the above-described reaction solution was poured into a polypropylene mold cell for a lens of a base curve of 9.0 mm, a size of 13.5 mm, a power of -3.00 diopters and a central thickness of 0.09 mm, said cell was irradiated for approximately 15 minutes with ultraviolet rays at a temperature of 40 to 50°C and a transparent copolymer was

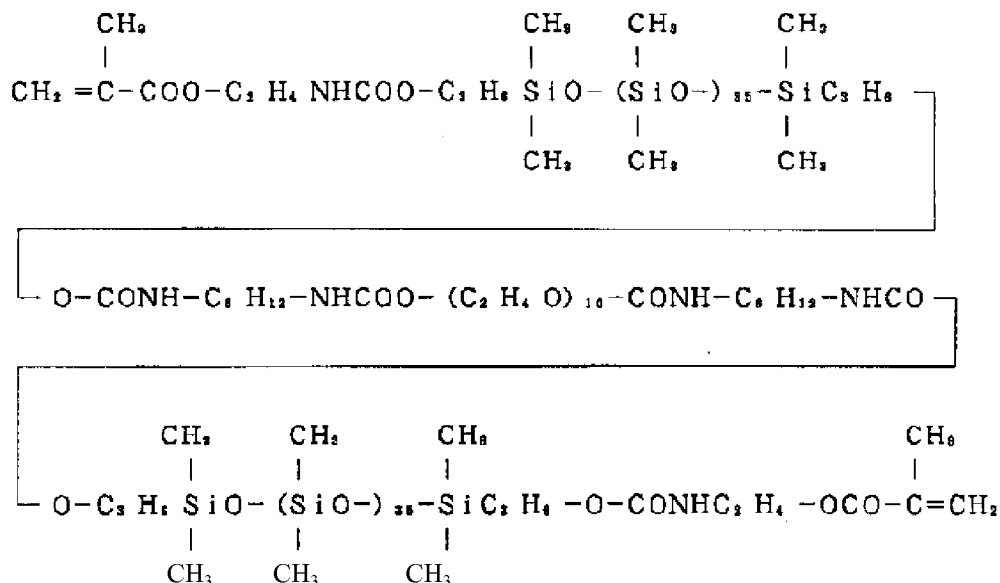
obtained. The copolymer that was obtained in this way was immersed and swollen in purified water at 90°C and was then further swollen in purified water at 70°C, with a water containing soft lens being obtained. In addition, a lens-shaped water-containing substance of a power of 0.0 diopters was obtained in the same way. The water-content ratio was 28%, the oxygen permeability coefficient was 150, the contact angle was 26°, tensile strength was 216 g/mm<sup>2</sup>, and protein and lipid soiling attachment were 5 µg/lens and 30 µg/lens.

[0035]

[Working Example 2]

[Chemical Formula 8]

[Chemical Formula 6]

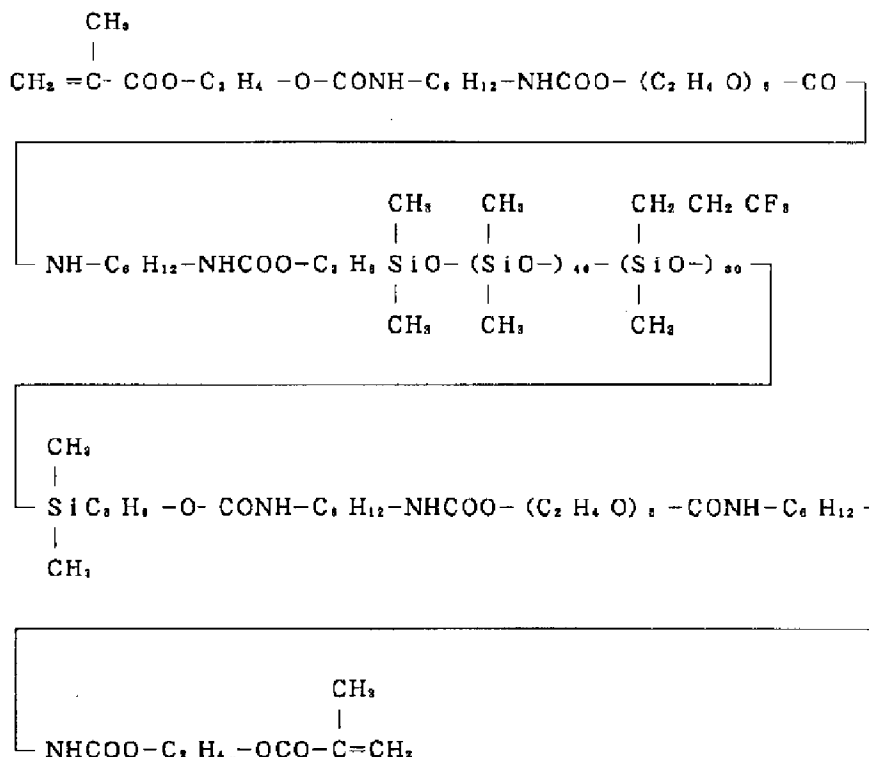


Organic siloxane diol was reacted and purified in the same way as in Working Example 1 and an organic siloxane macromer containing urethane and represented by Chemical Formula 7 below was obtained.

[0036]

[Chemical Formula 9]

[Chemical Formula 7]



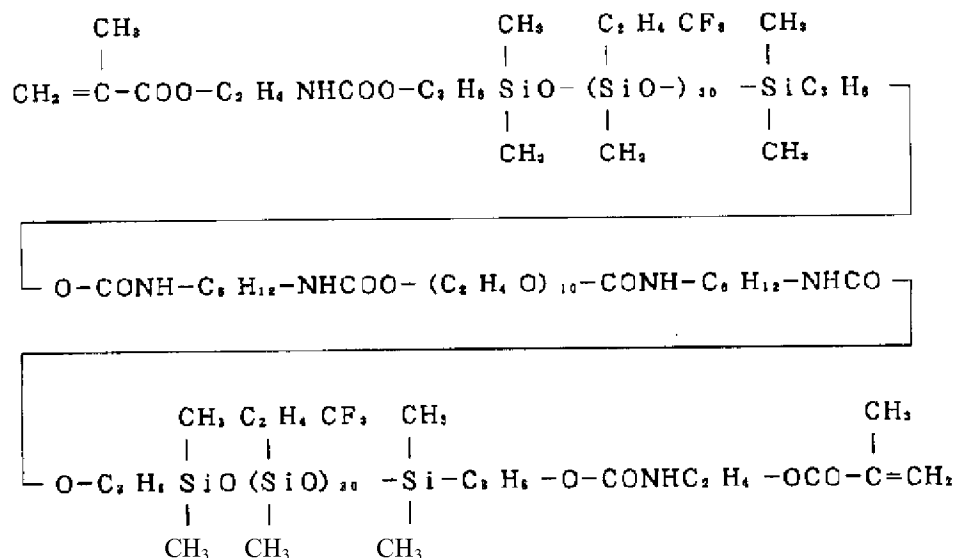
[0037] The macromer containing urethane bonds indicated Chemical Formula 6 above was obtained by reacting a corresponding siloxane diol with a polyethylene glycol diisocyanate compound and 2-isocyanato ethyl methacrylate by a method based on the method described in Working Example 1. 30 parts by weight of the organic siloxane macromer of Chemical Formula 7, 25 parts by weight of the

organic siloxane macromer of Chemical Formula 6, 15 parts by weight of tris(trimethylsiloxy) silyl propyl methacrylate, 15 parts by weight of N-vinyl pyrrolidone, 15 parts by weight of N,N'-dimethyl acrylamide, 15 parts by weight of trifluoroethyl methacrylate, 1 part by weight of ethylene glycol dimethacrylate and 0.5 parts by weight of benzyl dimethyl ketanol (brand name: I-651, manufactured by the

Ciba-Geigy Company) were added, and the mixture was dissolved and mixed for approximately 1 hour in a nitrogen atmosphere with a magnetic stirrer.

[0038] Following that, the above-described reaction solution was poured into polypropylene mold cell for the lens of a base curve of 9.0 mm, a size of 13.5 mm, a power of -3.00 diopters and a central thickness of 0.09 mm, said cell was irradiated for approximately 15 minutes with ultraviolet rays at a temperature of 40 to 50°C and a transparent copolymer was obtained. The copolymer that was obtained in this way was immersed and swollen in purified water at 90°C and was then further swollen in purified water at 70°C, with a water

[Chemical Formula 8]



[0040] Organic siloxane diol was reacted with 2 times its volume of 2-isocyanatoethyl methacrylate in the same way as in Working Example 2 and the mixture was purified, with the organic siloxane containing urethane bonds as indicated by Chemical Formula 8 being obtained. 55 parts by weight of the organic siloxane macromer containing urethane bonds as indicated by the above-described Chemical Formula 7, 20 parts by weight of the organic siloxane macromer indicated by Chemical Formula 8, 15 parts by weight of tris(trimethylsiloxy) silyl propyl methacrylate, 15 parts by weight of N-vinyl pyrrolidone, 15 parts by weight of N,N'-dimethyl acrylamide, 5 parts by weight of trifluoroethyl methacrylate, 1 part by weight of ethylene glycol dimethacrylate and 0.5 parts by weight of benzyl dimethyl ketanol (brand name: I-651, manufactured by the Ciba-Geigy Company) were added, and the mixture was dissolved and mixed for approximately 1 hour in a nitrogen atmosphere with a magnetic stirrer.

[0041] Following that, the above-described reaction solution was poured into polypropylene mold cell for the lens of a base curve of 9.0 mm, a size of 13.5 mm, a power of -3.00

containing soft lens being obtained. In addition, a lens-shaped water-containing substance of a power of 0.0 diopters was obtained in the same way. The water-content ratio was 30%, the oxygen permeability coefficient was 155, the contact angle was 22°, tensile strength was 216 g/mm<sup>2</sup>, and protein and lipid soiling attachment were 4 µg/lens and 20 µg/lens.

[0039]

[Working Example 3]

[Chemical Formula 10]

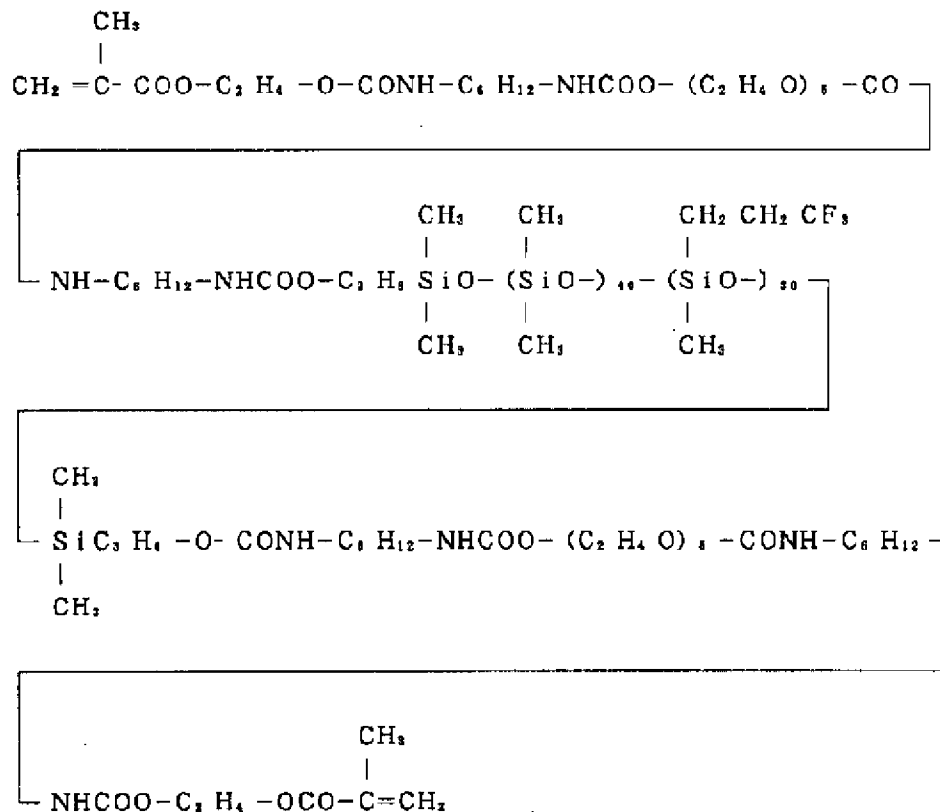
diopters and a central thickness of 0.09 mm, said cell was irradiated for approximately 15 minutes with ultraviolet rays at a temperature of 40 to 50°C and a transparent copolymer was obtained. The copolymer that was obtained in this way was immersed and swollen in purified water at 90°C and was then further swollen in purified water at 70°C, with a water containing soft lens being obtained. In addition, a lens-shaped water-containing substance of a power of 0.0 diopters was obtained in the same way. The water-content ratio was 20%, the oxygen permeability coefficient was 160, the contact angle was 22°, tensile strength was 214 g/mm<sup>2</sup>, and protein and lipid soiling attachment were 5 µg/lens and 15 µg/lens.

[0042]

[Working Example 4]

[Chemical Formula 11]

[Chemical Formula 7]



[0043] Organic siloxane diol was reacted with 2 times its volume of 2-hydroxyethyl methacrylate in the same way as in Working Example 1 and the mixture was purified, with the organic siloxane containing urethane bonds as indicated by Chemical Formula 7 being obtained. 55 parts by weight of the organic siloxane macromer containing urethane bonds as indicated by the above-described Chemical Formula 7, 15 parts by weight of tris(trimethylsiloxy) silyl propyl methacrylate, 15 parts by weight of N-vinyl pyrrolidone, 15 parts by weight of N,N'-dimethyl acrylamide, 5 parts by weight of trifluoroethyl methacrylate, 1 part by weight of ethylene glycol dimethacrylate and 0.5 parts by weight of benzyl dimethyl ketanol (brand name: I-651, manufactured by the Ciba-Geigy Company) were added, and the mixture was dissolved and mixed for approximately 1 hour in a nitrogen atmosphere with a magnetic stirrer.

[0044] Following that, the above-described reaction solution was poured into polypropylene mold cell for the lens of a

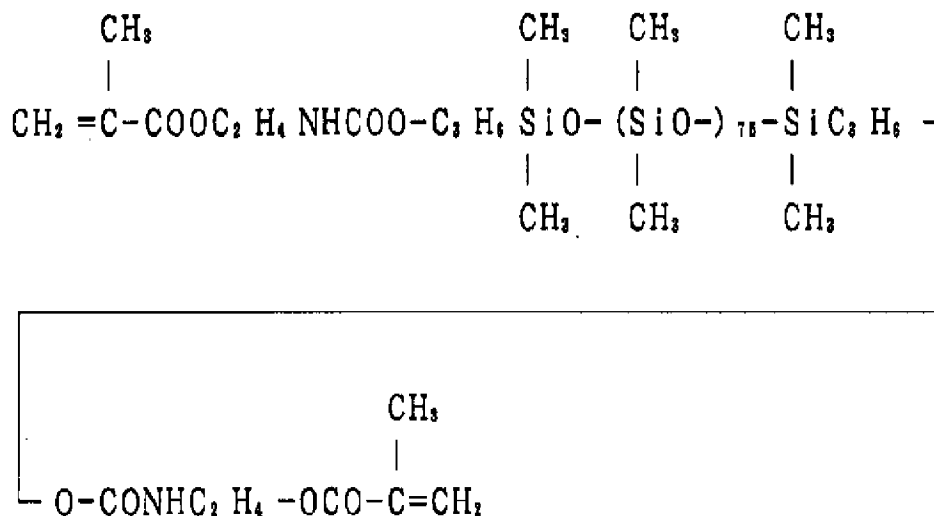
base curve of 9.0 mm, a size of 13.5 mm, a power of -3.00 diopters and a central thickness of 0.09 mm, said cell was irradiated for approximately 15 minutes with ultraviolet rays at a temperature of 40 to 50°C and a transparent copolymer was obtained. The copolymer that was obtained in this way was immersed and swollen in purified water at 90°C and was then further swollen in purified water at 70°C, with a water containing soft lens being obtained. In addition, a lens-shaped water-containing substance of a power of 0.0 diopters was obtained in the same way. The water-content ratio was 30%, the oxygen permeability coefficient was 165, the contact angle was 23°, tensile strength was 156 g/mm<sup>2</sup>, and protein and lipid soiling attachment were 3.0 µg/lens and 18 µg/lens.

[0045]

[Comparative Example 1]

[Chemical Formula 12]

[Chemical Formula 9]



[0046] Organic siloxane diol was reacted with 2 times its volume of 2-isocyanatoethyl methacrylate in the same way as in Working Example 2 and the mixture was purified, with the organic siloxane containing urethane bonds as indicated by Chemical Formula 9 being obtained. 55 parts by weight of the organic siloxane macromer containing urethane bonds as indicated by the above-described Chemical Formula 9, 15 parts by weight of tris(trimethylsiloxy) silyl propyl methacrylate, 15 parts by weight of N-vinyl pyrrolidone, 15 parts by weight of N,N'-dimethyl acrylamide, 5 parts by weight of trifluoroethyl methacrylate, 1 part by weight of ethylene glycol dimethacrylate and 0.5 parts by weight of benzyl dimethyl ketanol (brand name: I-651, manufactured by the Ciba-Geigy Company) were added, and the mixture was dissolved and mixed for approximately 1 hour in a nitrogen atmosphere with a magnetic stirrer. Following that, the above-described reaction solution was poured into a polypropylene mold cell for the lens of a base cover of 9.0 mm, a size of 13.5 mm, a power of -3.00 diopters and a central thickness of 0.09 mm, said cell was irradiated for approximately 15 minutes with ultraviolet rays at a temperature of 40 to 50°C and a transparent copolymer was obtained.

[0047] The copolymer that was obtained in this way was immersed and swollen in purified water at 90°C and was then further swollen in purified water at 70°C, with a water containing soft lens being obtained. In addition, a lens-shaped water-containing substance of a power of 0.0 diopters was obtained in the same way. The water-content ratio was 25%, the oxygen permeability coefficient was 250, the contact angle was 27°, tensile strength was 156 g/mm<sup>2</sup>, and protein and lipid soiling attachment were 30 µg/lens and 35 µg/lens. This lens was installed for 21 days in the eyes of a domestic rabbit. There was a large amount of lipid soiling, the lens exhibited white turbidity and the wettability of the recovered lens was poor. When the lens was removed from the storage solution, there was no aqueous phase on the lens surface. In addition, the lens was greatly swollen and absorption of lipids was found.

[0048]

[Effect of the Invention] The contact lens material of this invention is a material of superior soiling attachment properties and of a superior balance of physical properties such as oxygen permeability and mechanical strength.

Continued from front page

F Terms (Reference)	2H006	BB01	BB05	BB07
	4J027	AA02	AF05	AF06
		BA07	BA08	BA12
			BA14	BA19
			BA20	BA21
			CD04	